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[redacted]-TR-88007

[redacted] MATERIALS FROM 60-mm MORTAR OBTURATORS

[redacted] Zdyrski

[redacted] 1988

[redacted] RESEARCH, DEVELOPMENT AND
[redacted] ENGINEERING CENTER

[redacted] Engineering Directorate
[redacted], Armament, New Jersey

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER) Technical Report ARAED-TR-88007	5. MONITORING ORGANIZATION REPORT NUMBER)
6a. NAME OF PERFORMING ORGANIZATION ARDEC, AED Armaments Technology Div 6b. OFFICE SYMBOL SMCAR-AET	7a. NAME OF MONITORING ORGANIZATION ARDEC, FSAC Artillery Armaments Div (SMCAR-FSA)
6c. ADDRESS (CITY, STATE, AND ZIP CODE) Picatinny Arsenal, NJ 07806-5000	7b. ADDRESS (CITY, STATE, AND ZIP CODE) Picatinny Arsenal, NJ 07806-5000
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ARDEC, IMD STINFO Br 8b. OFFICE SYMBOL SMCAR-IMI-I	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (CITY, STATE, AND ZIP CODE) Picatinny Arsenal, NJ 07806-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (INCLUDE SECURITY CLASSIFICATION)

IDENTIFICATION OF MATERIALS FROM 60-mm MORTAR OBTURATORS

12. PERSONAL AUTHOR(S)
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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (YEAR, MONTH, DAY)	15. PAGE COUNT
Technical	FROM _____ TO _____	July 1988	26

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (CONTINUE ON REVERSE IF NECESSARY AND IDENTIFY BY BLOCK NUMBER)		
FIELD	GROUP	SUB-GROUP	Polycarbonate;	Thermal analysis;	Plastic;
			Acetal resin;	Formaldehyde resin;	Obturator;
			Ammunition	Infrared analysis	

19. ABSTRACT (CONTINUE ON REVERSE IF NECESSARY AND IDENTIFY BY BLOCK NUMBER)

Two plastic obturators for the 60-mm mortar were submitted for physical and chemical analysis. One of the obturators was from current U.S. Army stock while the other was from a contractor which had failed by misfire during field tests. The analysis revealed their composition to be polycarbonate and acetal polymer resins, respectively. This report discusses in detail the physical and chemical analysis and presents the results obtained together with conclusions and recommendations.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL I. HAZNEDARI	22b. TELEPHONE (INCLUDE AREA CODE) (201)724-3316
	22c. OFFICE SYMBOL SMCAR-IMI-I

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INTRODUCTION

Two plastic obturators, green and white from the 60-mm mortar, were submitted for analysis. The green obturator was from current U.S. Army stock while the white obturator was obtained from a contractor which has failed by misfire at a high temperature (110°F) during field tests.

This investigation was to determine the composition of the obturators with respect to the binding resin, filler, chemical structure, and key physical properties.

RESULTS OF PHYSICAL EXAMINATION AND ANALYSIS

The two obturators were identified by their external coloration and were physically tested with the following results:

Obturator	Specific gravity at 25°C	Relative toughness and breaking strength (by visual examination)
green	1.213	Very tough and could not be broken
white	1.520	Very hard and could be broken easily

NOTE: For comparison, the reported density of polycarbonate is 1.2 and Delrin® is 1.4.

Careful visual examination of the two obturators revealed that only the green obturator was transparent indicating that it had no inorganic filler.

To determine their composition, both obturators were tested for solubility, ash content, by thermogravimetry (TG) and by infrared spectrophotometric analysis (IR) using three different sample preparation.

Solubility Tests

The obturators were tested for solubility in a wide range of polar and non-polar solvents to determine a clue as to their identity and to develop a method for extraction of the resin binder for forming a thin resin film for the infrared analysis. The green obturator was insoluble in toluene, ethyl acetate, and acetone but soluble in chloroform and methylene chloride which suggested a polycarbonate resin. The white obturator was insoluble in toluene, ethyl acetate, 90% formic acid, methylene chloride, dimethyl formamide, benzene, chloroform, tetrahydrofurane, methanol, acetonitrile, acetic anhydride, and chloroform. Although the white obturator was soluble in boiling dimethylformamide and boiling orthodichlorbenzene (which precipititated rapidly from solution on cooling), it is believed that thermal degradation of the polymer took place during the boiling since a polymer film could not be cast from the hot solution onto a heated glass plate for

the infrared analysis. This conclusion is based on the discoloration and observed brittleness of the film deposited on the glass.

The boiling point of dimethylformamide is 153°C and ortho-dichlorobenzene is 181°C. A literature search suggested that this high degree of insolubility might be due to the presence of an acetal resin or a long chain nylon material.

Upon dissolving the white obturator in the hot dimethyl formamide and ortho-dichlorobenzene, the white component appeared to be a very finely powedered pigment or filler which did not settle and separate readily.

Ash Content

The inorganic ash content of the obturator samples was obtained directly from the thermogravimetry (TG) thermal curves which were run from 100°C to 800°C over a nitrogen atmosphere followed by air (oxygen) to burn off any remaining carbon residue. The results were rechecked by a second run on each sample using air over the entire determination. Only the white obturator contained an ash residue (20%) (figs. 1, 2, 4, and 5).

Thermogravimetry

TG is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere (in this case, nitrogen followed by air which would supply the necessary oxygen to burn off any carbon residue remaining after the completion of the thermal decomposition).

By using this method, it was observed that the rate of mass loss of the samples was measured in milligrams per minute as the obturator materials were subjected to a programmed range of temperature rise in a dynamic inert nitrogen atmosphere followed by air (oxygen). No lower temperature volatilization in the sample was observed that might indicate contamination or the presence of unreacted monomer or premature thermal breakdown. True thermal decomposition was also determined under dynamic nitrogen in which the sustained flow of the fresh inert gas would insure the continual removal of thermal composition products without the possibility of oxidation of the sample also occurring. After all thermal decomposition was completed, air was substituted for the nitrogen to provide oxygen to burn off any carbon residue which may have formed during the thermal decomposition. This provided information on the inorganic ash and filler content of the obturator samples.

Green Obturator

The decomposition of the green obturator under nitrogen followed by air which burned off any residual carbon formed by the initial decomposition is shown in figure 1, a thermal run in dynamic air in figure 2. The decomposition occurs sooner in the air run. A known polycarbonate fuze cover which was run for comparison against the thermal curves of the

green obturators (fig. 3) had a slightly lower decomposition temperature which may be due to an anomaly in the polycarbonate and/or additive heat stabilizers.

White Obturator

The decomposition of the white obturator under nitrogen followed by air which burned off any residual carbon formed by the initial decomposition is shown in figure 4; a thermal run in dynamic air in figure 5. As in the green obturator, the decomposition occurs sooner and at a faster rate. Two different known acetal resin runs which were plotted for comparison against the thermal curves of the white obturator are shown in figures 6 and 7. The two knowns had slightly lower decomposition temperatures which again may be due to the presence of an anomaly in the acetal resin and/or additive heat stabilizers.

The Perkin Elmer Model TGS-2 thermogravimetric analyzer with the Perkin Elmer thermal analysis data station/system 4 computer was used in this investigation which was accurately calibrated/checked before and after the determinations using the magnetic transition temperatures (Curie points) of nickel (534°C) and iron (780°C). The Curie points are the temperatures at which ferromagnetic materials lose their magnetic properties as a result of the disorientation of their magnetic domains and transforming to the paramagnetic state. This provides for a relatively accurate temperature calibration standard. It is the only method by which the temperature of the interior of the sample pan can be determined since the thermal plot only represents the thermocouple temperature which is actually outside and about 2 mm below the sample pan (fig. 8).

The onset of decomposition is determined at the intersection of a straight line extension tangent to the steepest slope decent of the decomposition with the base line prior to the decomposition. The actual decomposition starts somewhat before the onset temperature.

Infrared Spectrophotometric Analysis

Before infrared analysis could be attempted, it was necessary to dissolve the obturator material and cast an approximately 1- to 3-mil thick film which would be able to transmit all of the infrared radiation in the 450 to 4000 wave number range. As pointed out earlier, only the resin from the green obturator dissolved readily in methylene chloride at room temperature from which a thin IR transmitting film could be cast that was acceptable for infrared analysis. An acceptable infrared spectrum was obtained from this film.

The white obturator was found to only be soluble in boiling dimethylformamide and boiling orthodichlorobenzene after an hour of heating. Since the sample precipitated rapidly from the solution on cooling, it was not possible to form a good film even when pouring the solution onto a heated piece of glass. It also appeared that the heating caused a degradation of the polymer. After several unsuccessfuly attempts, this method of sample preparation was abandoned.

By taking advantage of the fact that the obturator material was white giving good reflectance, shavings from the sample were prepared and a diffuse reflectance spectrum of fair quality was obtained after several attempts using the IR diffuse reflectance accessory.

Still another sample preparation attempt was made with the white obturator by melt smearing the obturator onto a hot KRS-5 crystal to form a thin film and cooling immediately to minimize thermal degradation. After several unsuccessful attempts, a relatively good film was made from which a good quality IR spectrum was obtained.

An acceptable IR spectrum requires that the absorption bands are prominent but not in contact with the 0% IR transmission base line. This is an important prerequisite for the quality spectrum processing and the analysis which follows.

Spectrum Processing

The samples were placed in the Perkin Elmer model 1750 fourier transform infrared (FTIR) and an IR spectrum obtained which was further computer enhanced by the application of an absorbance expansion factor (ABEX) which is a means of proportionally simulating on an IR spectrum, a change in sample thickness (or concentration) within certain ordinate limits. The spectrum was further computer processed by a 13-point smoothing factor according to the Savitztky/Golay process to eliminate unwanted noise and many nonpertinent small peaks in the IR spectrum. A curved flattening factor was also applied to correct for any sloping of the IR plot. The IR spectrum was now ready for a computer analysis, spectral interpretation and a library search (figs. 9 through 11).

Spectral Interpretation and Search

A peak table was derived from the spectrum which lists all the peak absorbances with corresponding spectrum frequencies by wave number with percent transmittance. These data were then interpreted by computer as to the possible chemical structural units. The peak table along with the chemical interpretation was then compared and searched by computer to peak tables stored in the hard disk of our polymer spectral library containing 1600 polymeric compounds. The best matches in descending order of best fit between the sample peak table and each of the library peak tables were obtained (tables 1 through 3). The search was conducted under 4 different scoring algorithms with the 26 closest matches obtained, each in descending order of "best fit". A scoring of 9-9 is a perfect match while a 0-0 is the lowest score. The left hand score is for the chemical structural units while the right hand score is for the peak-to-peak match. The IR spectrums having the highest scores were selected and their reference spectrums obtained from our library volumes.* The reference IR spectrums were matched with the IR

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* Atlas of Polymers and Plastics Analysis, Vol 1, "Polymers, Structures, and Spectra," Prof. Dr. Dieter O. Hummel, Cologne, pp 241, 437, and 439, 1982.

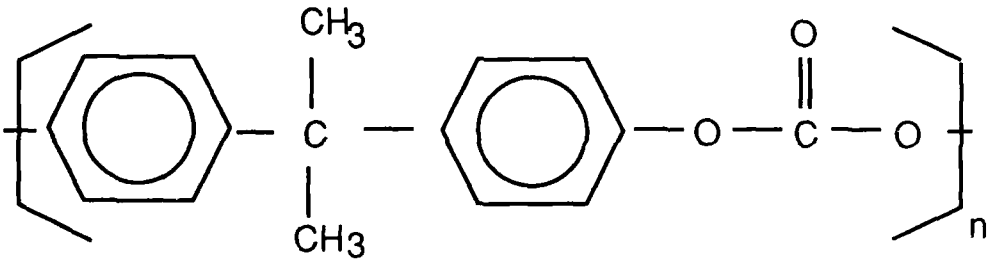
spectrums obtained from the samples. Since the sample films were contaminated with dyes, stabilizers, and other impurities, it would be expected that some IR absorption interference could be anticipated resulting in a slightly altered spectrum, interpretation, and math. In addition, polymer heat degradation during sample preparation especially in the case of the white obturator could alter the IR spectrum considerably.

INTERPRETATION OF DATA

Green Obturator

Based upon the computer search and scoring (9-8) polycarbonate from bis (4-hydroxyphenyl)-2-propane from the "peak" scoring algorithm gave an almost a perfect score match. Visual comparison of the sample IR spectrum against out volume reference spectrums gave a very good match for polycarbonate from bis (4-hydroxyphenyl)-2-propane except for a few minor IR absorptions probably attributable to the green dye or other polymer additives. Other second match candidates are listed in the computer search.

This polymer is synthesized from bisphenol acetone and phosgene. The chemical structure of this polycarbonate polymer is:



White Obturator

Since it was not possible to cast a good thin film from this material, two spectrums were obtained by two different sample preparation/spectrum methods (diffuse reflectance and hot melt smear). Both spectrums and computer searches were considered in the evaluation. The fact that both computer searches yielded acetal resin poly (oxymethylene) and polyether-1 as the best match (tables 2 and 3) (with one scoring 9-8) confirms that the principal polymer of the white obturator is poly (oxymethylene), polyether 1 more commonly known as acetal resin. This material is a polymerization product of formaldehyde and has the following basic structural formula:

$- O [CH_2 - O]_n CH_2 -$

CONCLUSIONS

The green obturator is composed of a polycarbonate resin, tinted with a green dye. It does not contain any inorganic filler material and thermally decomposes initially at about 500°C. The density is 1.213 at 25°C. The material is strong and tough.

The white obturator is composed of acetal resin, poly (oxymethylene), polyether 1 which is a polymer of formaldehyde commonly known as Delrin. It is highly insoluble in practically all organic solvents and has a density of 1.520 at 25°C. It contains 20% inorganic filler. The material is hard and very brittle.

Based upon the above results it is easy to understand why the white obturator failed by misfire in field tests.

RECOMMENDATIONS

It is recommended that the following supplemental analytical information be obtained. This information would quantify the total composition analysis of the two obturators and provide information on thermal expansion.

1. Complete the analysis of the white obturator by determining the composition of the white ash residue filler material.

2. Complete the thermal analysis of both obturator by obtaining thermal curves by differential scanning calorimetry on the samples. This information would provide plotted data on melting points, glass transition temperaturesm the rate of heat energy changes, crystallinity, and chemical/physical reactions occurring through a programmed temperature rise.

3. Determine the coefficient of thermal expansion of both the green and white obturators and compare the differences.

4. Based upon the results and conclusions, the white obturators are not recommended for use as ammunition obturators if optimum strength, toughness, and thermal properties are of prime consideration. The green polycarbonate obturators are far superior in strength, toughness, flexibility, and thermal properties.

Table 1. Computer search of infrared spectrum of green obturator (peak algorithm)

Search (peak) Page: 1 Band tolerance: 5 Thu Jan 07 15:37:32 1988
Peak Table: Region X Library: W4: Polymer lb

9-8	HU241C	Polycarbonate from Bis (4-hydroxphenyl)-2-propane
9-8	HU241C	Polycarbonate from Bis (4-hydroxphenyl)-2-propane
3-7	HU242A	Polycarbonate aromatic-aliphatic
6-6	HU577B	Dimethylsiloxane-bisphenol-a-carbonate block copolymer
9-5	HU577C	Bisphenol-a-carbonate-dimethylsiloxane block copolymer
9-5	HU577A	Dimethylsiloxane-bisphenol-a-carbonate block copolymer
9-2	HU432A	Polyurethane aromatic
9-1	HU239C	Polyester from bisphenol A, isophthal IC, terephthalic acids
9-1	HU241A	Polycondensate 4,5 (1, 1, 3-trimethyl-3-phenylindane dicarboxylic acid)
9-2	HU296C	Block copolymer bisphenol-A-terephthalate/oxyethylene sequences
9-2	HU619C	Ester ether sulfone, aromatic block copolymer

Chemical check failed list (chem: solid)

6-0	HU229C	Copolyester unsaturated from adipic/maleic/phthalic acids and diol
4-1	HU026C	Poly (propylene), cationic
3-2	HU002C	Ethene-propene copolymer

Table 2. Computer search of infrared spectrum of white obturator (by diffuse reflectance)

Search (peak) Page: 1 Band tolerance: 5 Mon Jan 11 15:34:26 1988
Peak Table: Region X Library: W4: Polymer lb

9-5	HU147A	Poly(oxymethylene), polyether-1
9-4	HU146B	Poly(oxymethylene), polyether-1
9-0	HU306C	Poly(thioethylene)
9-0	HU549B	Poly(thiophene-2,5-dicarboxylic hydrazine)
9-0	HU312A	Poly(thio-2-dimethylpropane)
9-0	HU039A	Poly(1-methylene ethylene), polyallene
9-0	HU080B	Tetrafluoroethylene, grafted onto polyethylene
6-3	HU147B	Trioxane-1,3-dioxolane copolymer
9-0	HU136C	Poly(4-vinyl-N-N-butylpyridiniumbromide)
9-0	HU004B	Ethene-4-methylpent-1-ene copolymer
9-0	HU146C	Poly(oxymethylene), polyether-1

Chemical check failed list (chem: solid)

9-0	HU016C	Poly(1-n-hexylethylene) isotactic (20 deg C)
6-1	HU026C	Poly(propylene), cationic
9-0	HU007C	Propene-ethene copolymer

Table 3. Computer search of infrared spectra of white obturator (hot melt smear)

Search (peak) Page: 1 Band tolerance: 5 Mon Jan 11 16:45:50
Peak Table: Region 2 Library: W4: Polymer lb

9-8	HU147A	Poly(oxymethylene), polyether-1
9-7	HU146B	Poly(oxymethylene), polyether-1
6-7	HU147B	Trioxane-1,3-dioxolane copolymer
3-7	HU074C	Acenaohthylene-trioxane copolymer
9-6	HU146C	Poly(oxymethylene), polyether-1
9-3	HU519A	Thiomethylenetri (oxymethylene) sodium carboxylate copolymer
9-0	HU312C	Poly (thio-1,4-phenylene)
9-0	HU312A	Poly (thio-2-dimethylpropane)
9-0	HU332B	Poly (epichlorohydrin); poly (oxy-1-chloromethylethylene)
9-0	HU164C	Poly (vinylstearylether)
9-0	HU004B	Ethene-4-methylpent-1-ene copolymer

Chemical check failed list (chem: solid)

9-0	HU587C	P-fluorophenylmethylsilicone-vinylmethylsilicone copolymer
6-1	HU595C	Poly (oxyhexamethyleneoxy-(hydrodenphosphinylidene))
6-0	HU026C	Poly (propylene), cationic

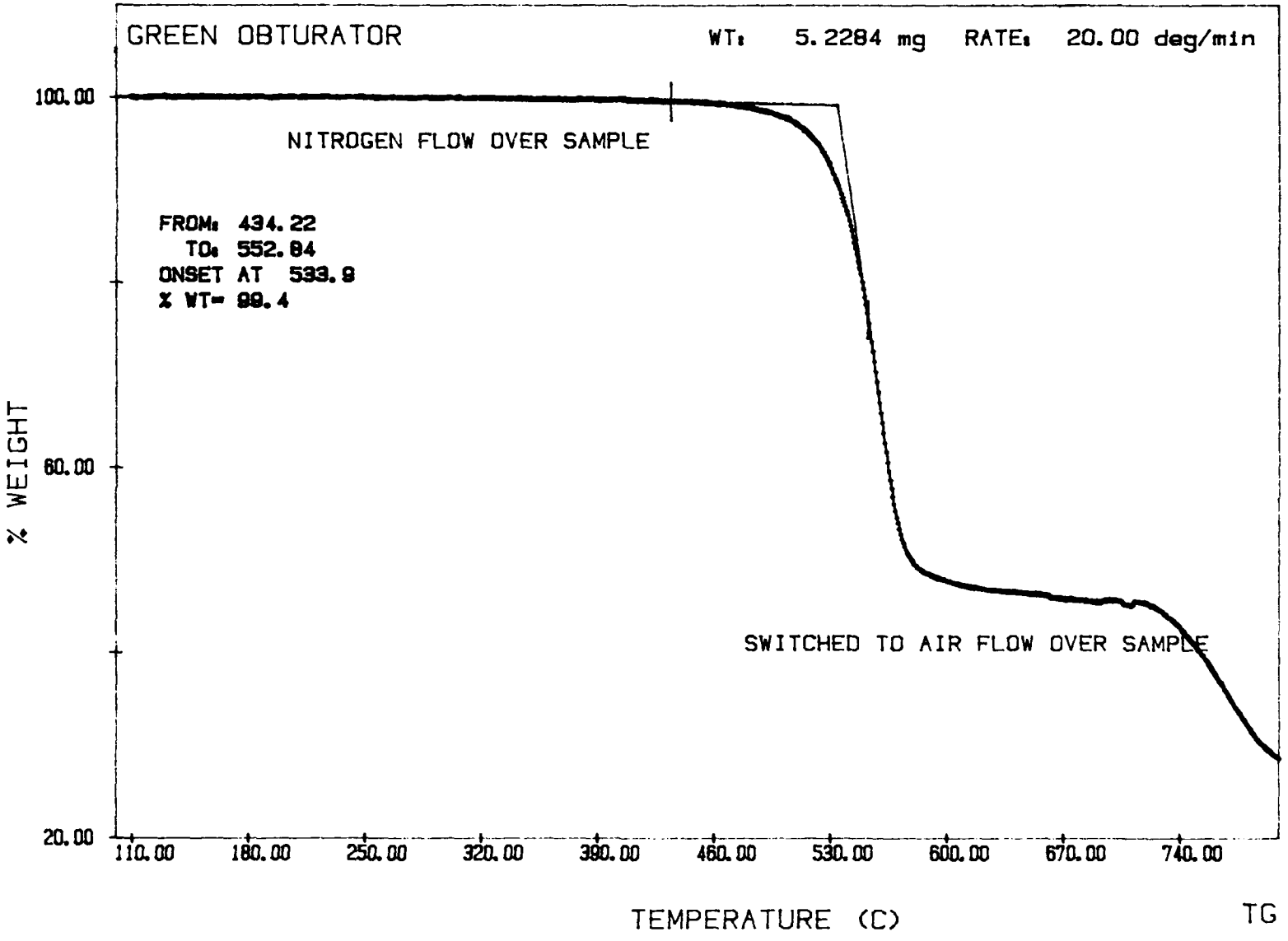


Figure 1. Thermogravimetry (TG) of the green obturator over nitrogen then air

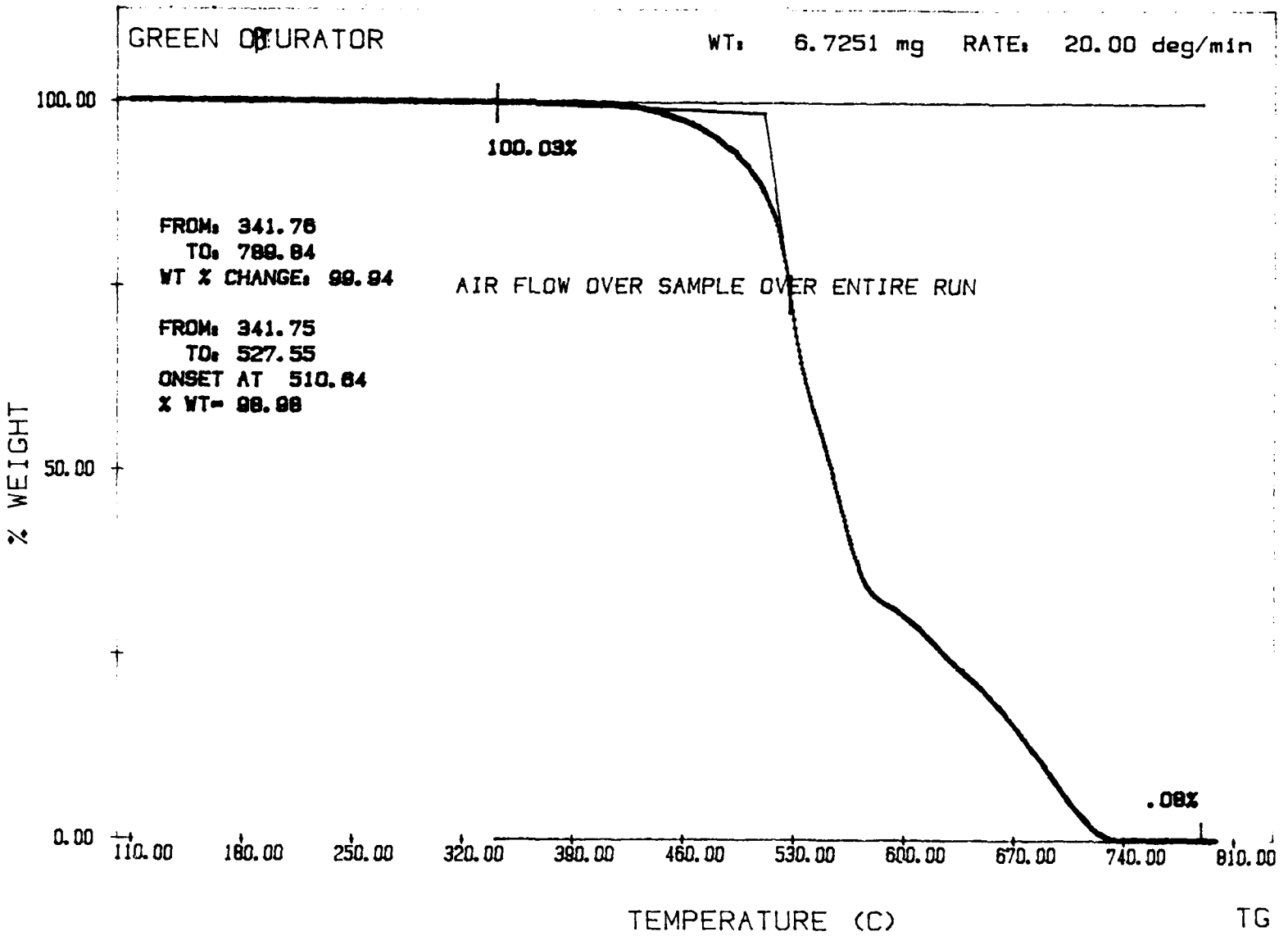


Figure 2. Thermogravity (TG) of the green obturator over air

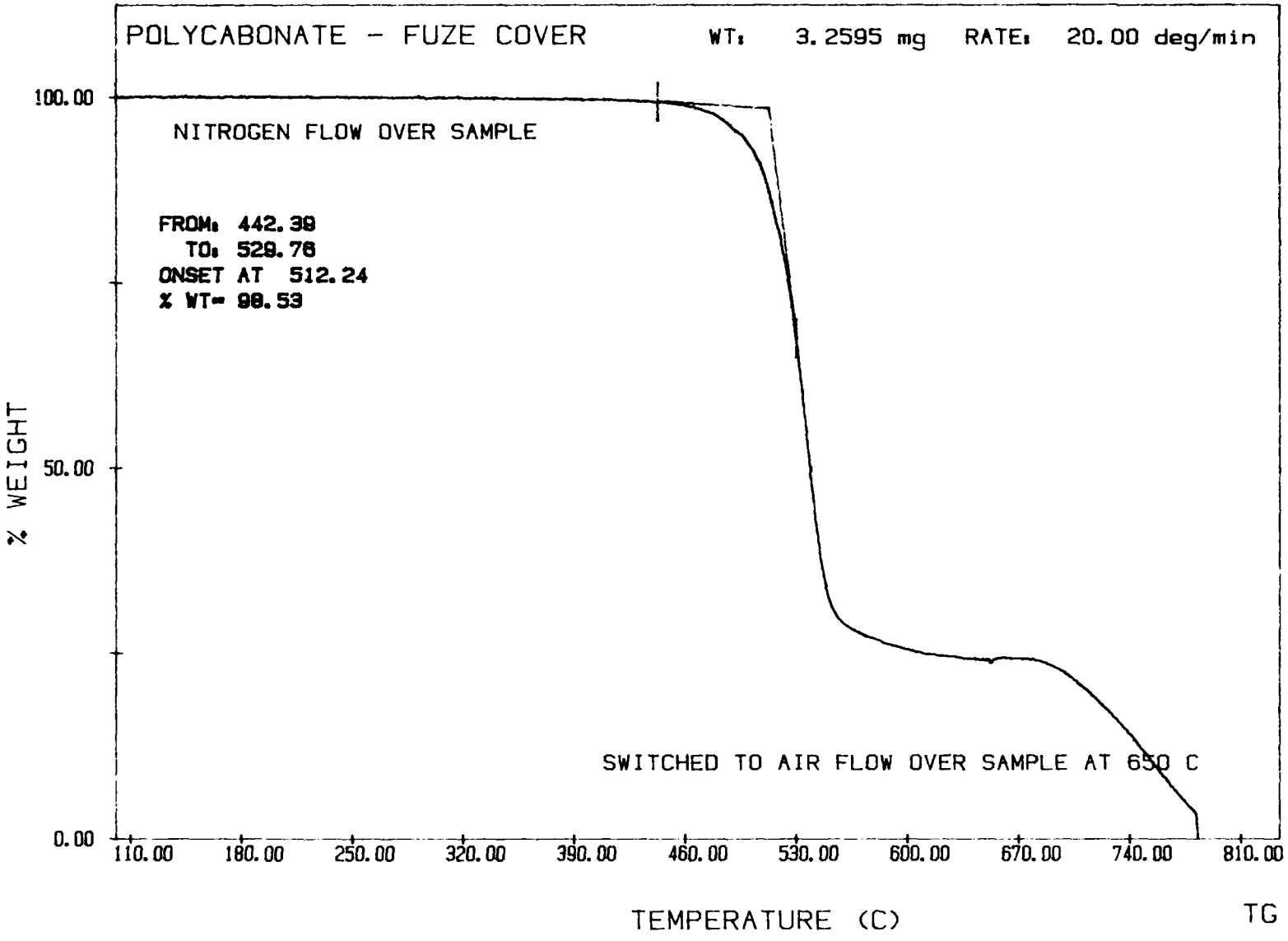


Table 3. Thermogravimetry (TG) of polycarbonate (fuze cover) over nitrogen then air

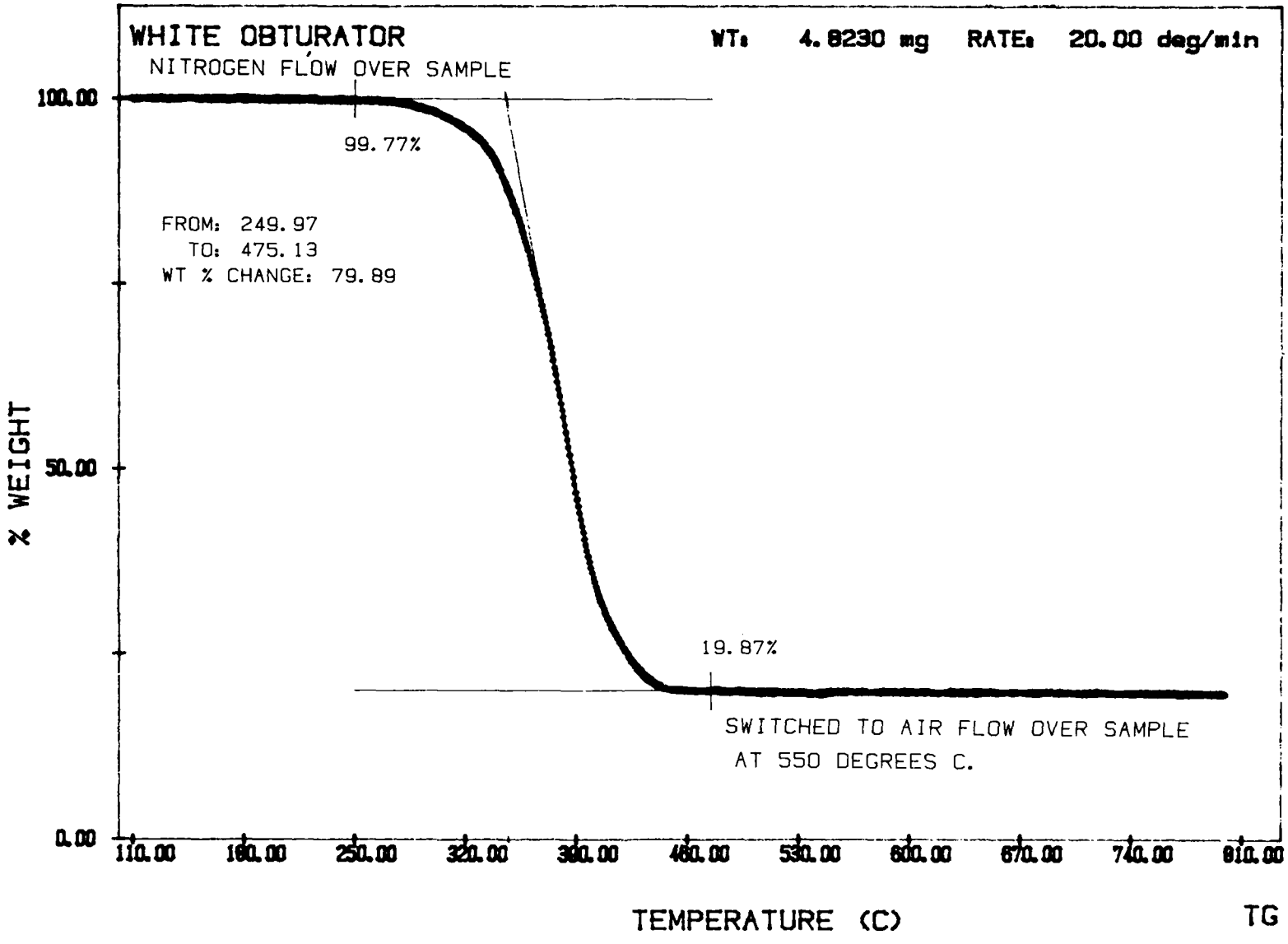


Figure 4. Thermogravimetry (TG) of the white obturator over nitrogen then air

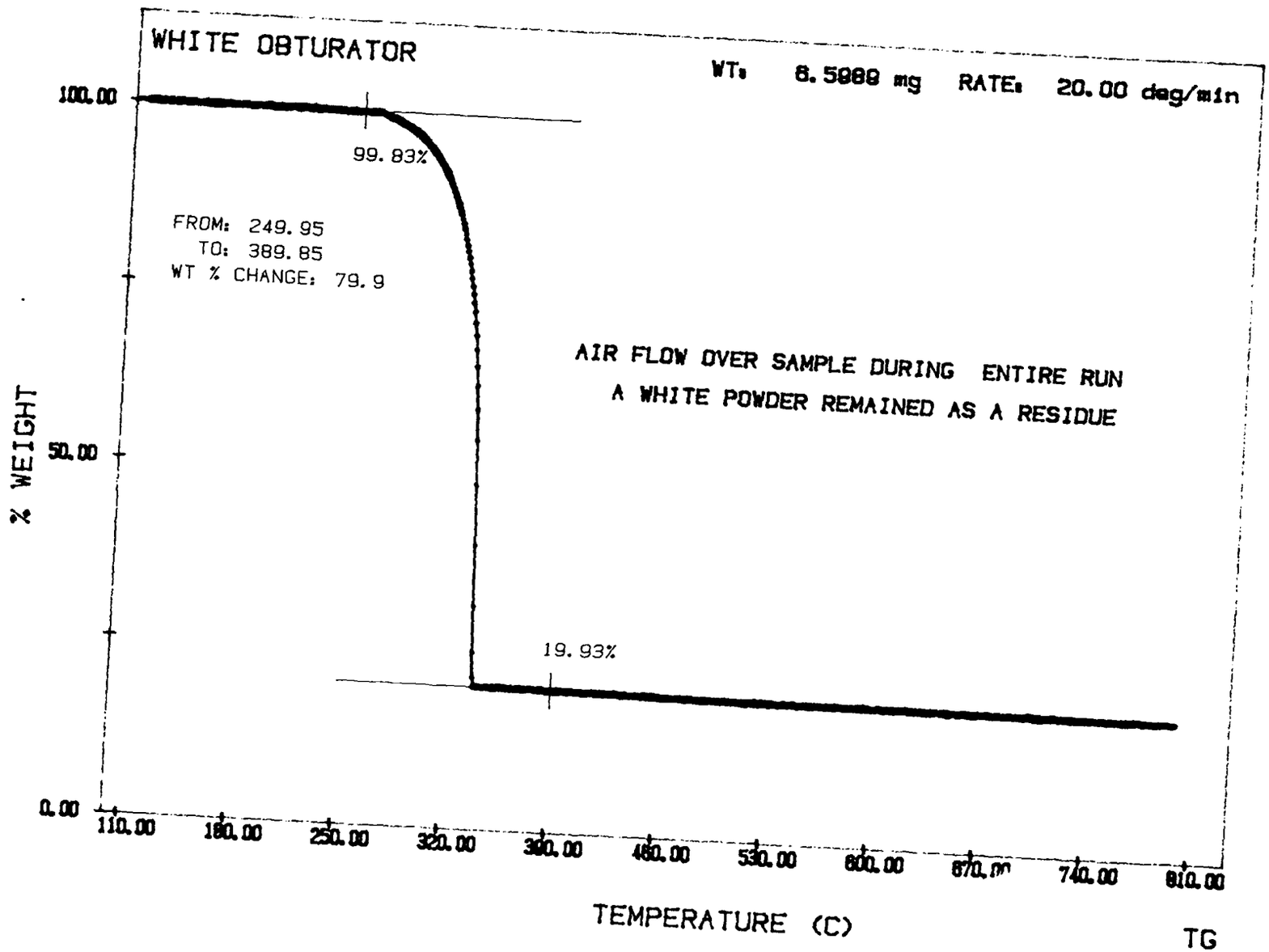


Figure 5. Thermogravity (TG) of the white obturator over air

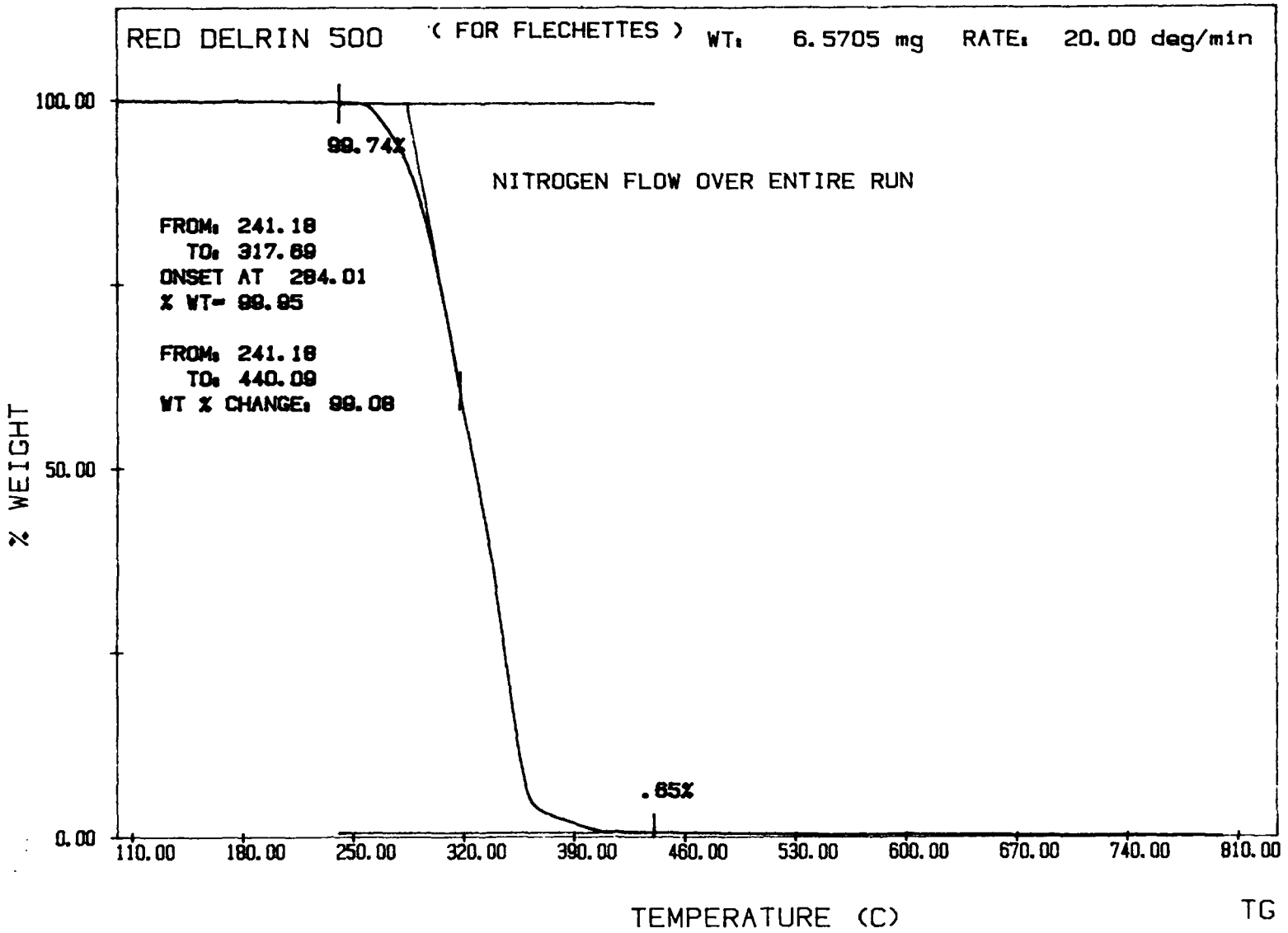


Figure 6. Thermogravimetry (TG) of red delrin 500 (from flechettes) over nitrogen

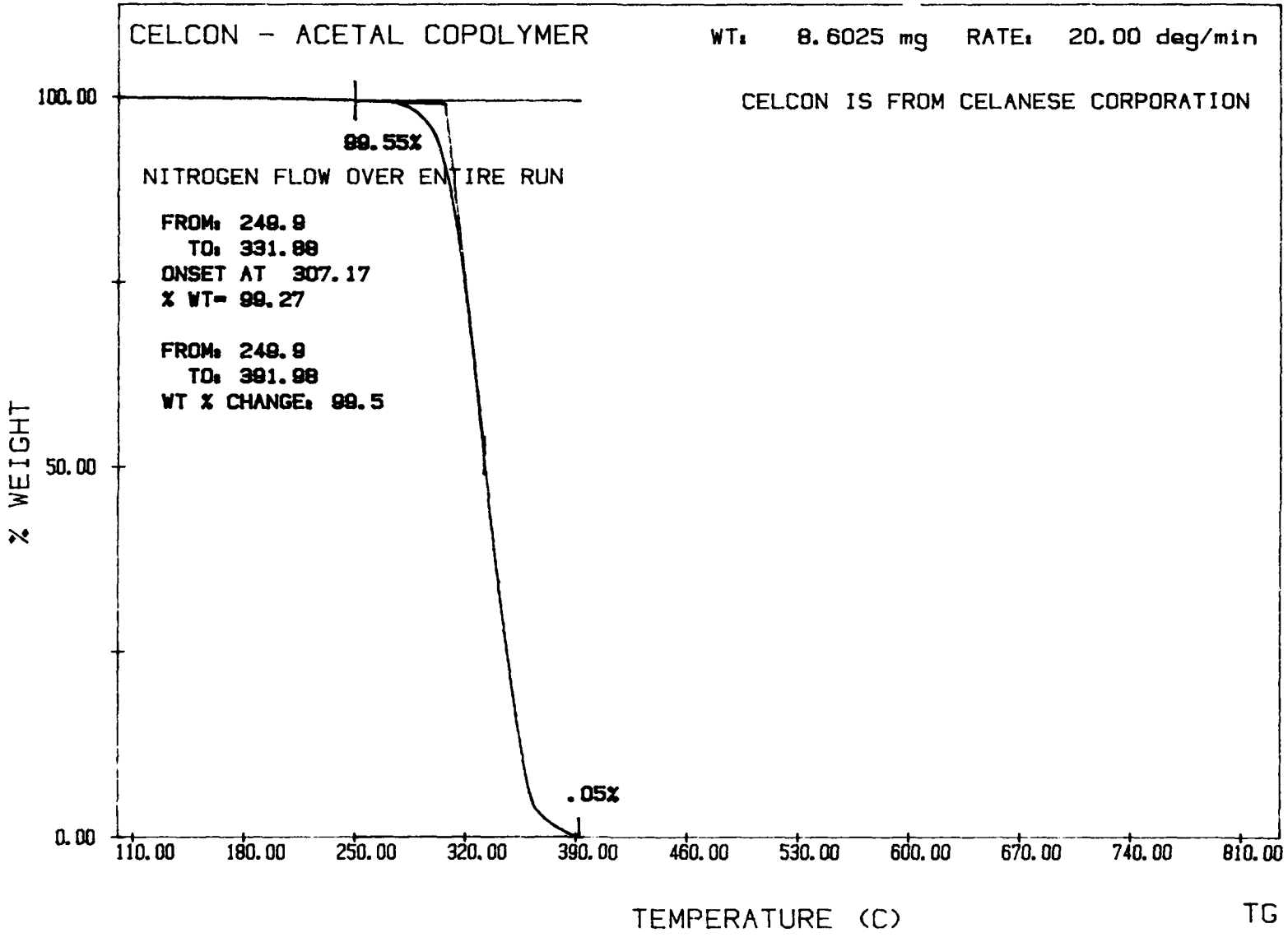


Figure 7. Thermogravimetry (TG) of celcon acetal copolymer over nitrogen

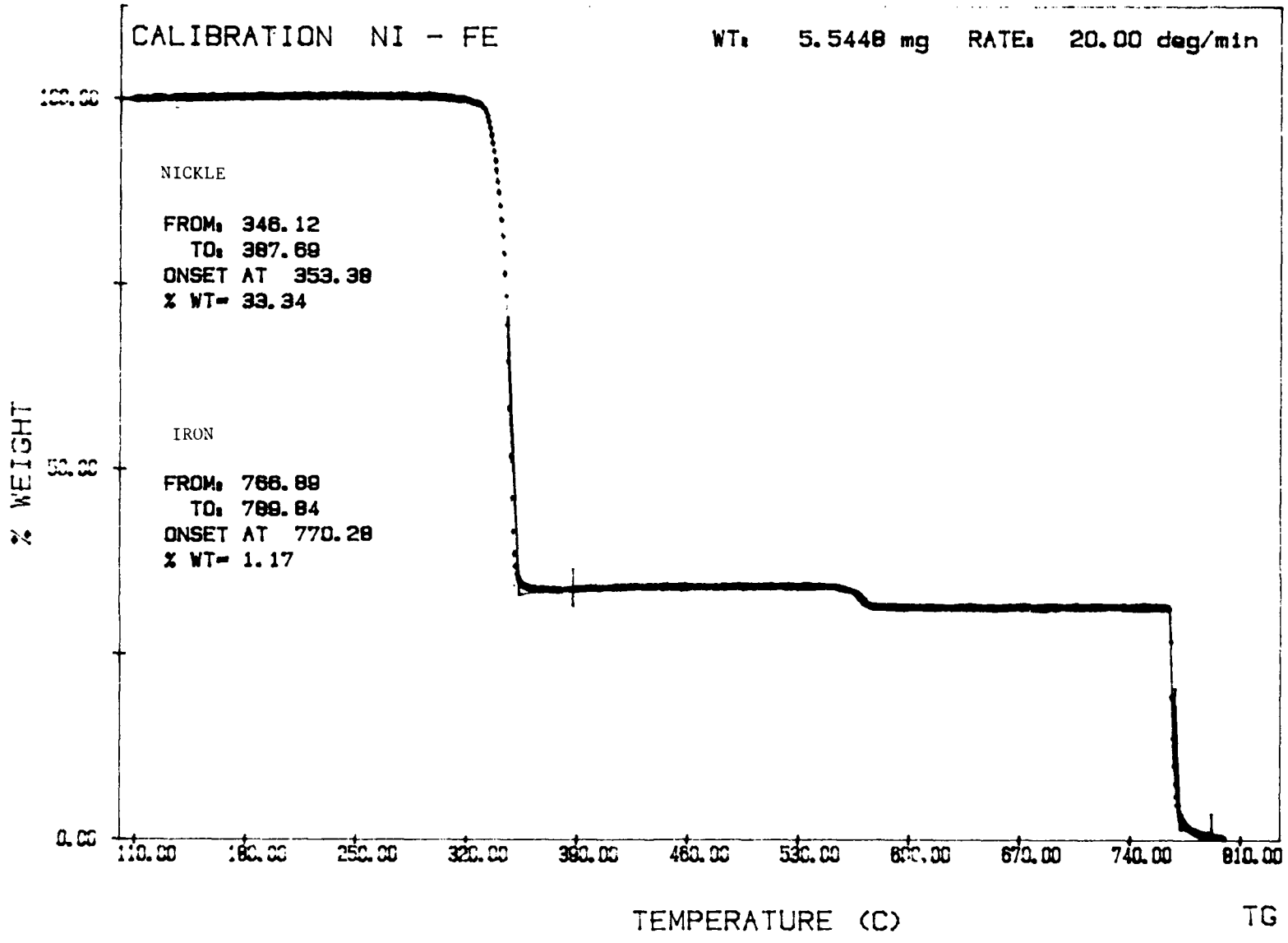


Figure 8. Thermogravimetry (TG) nickle/iron temperature calibration curves

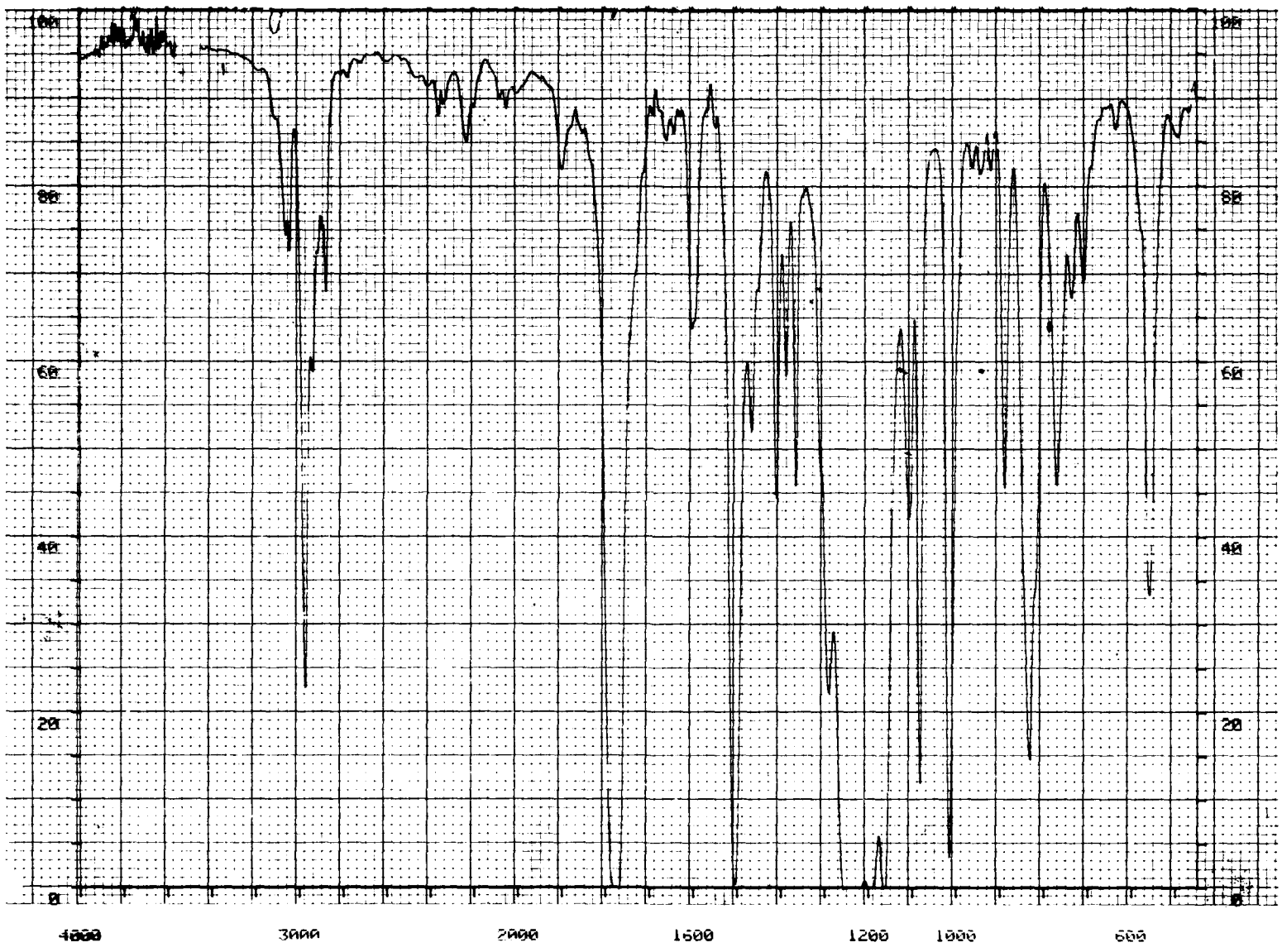


Figure 9. Infrared spectrum of green obturator (film cast from methylene chloride)

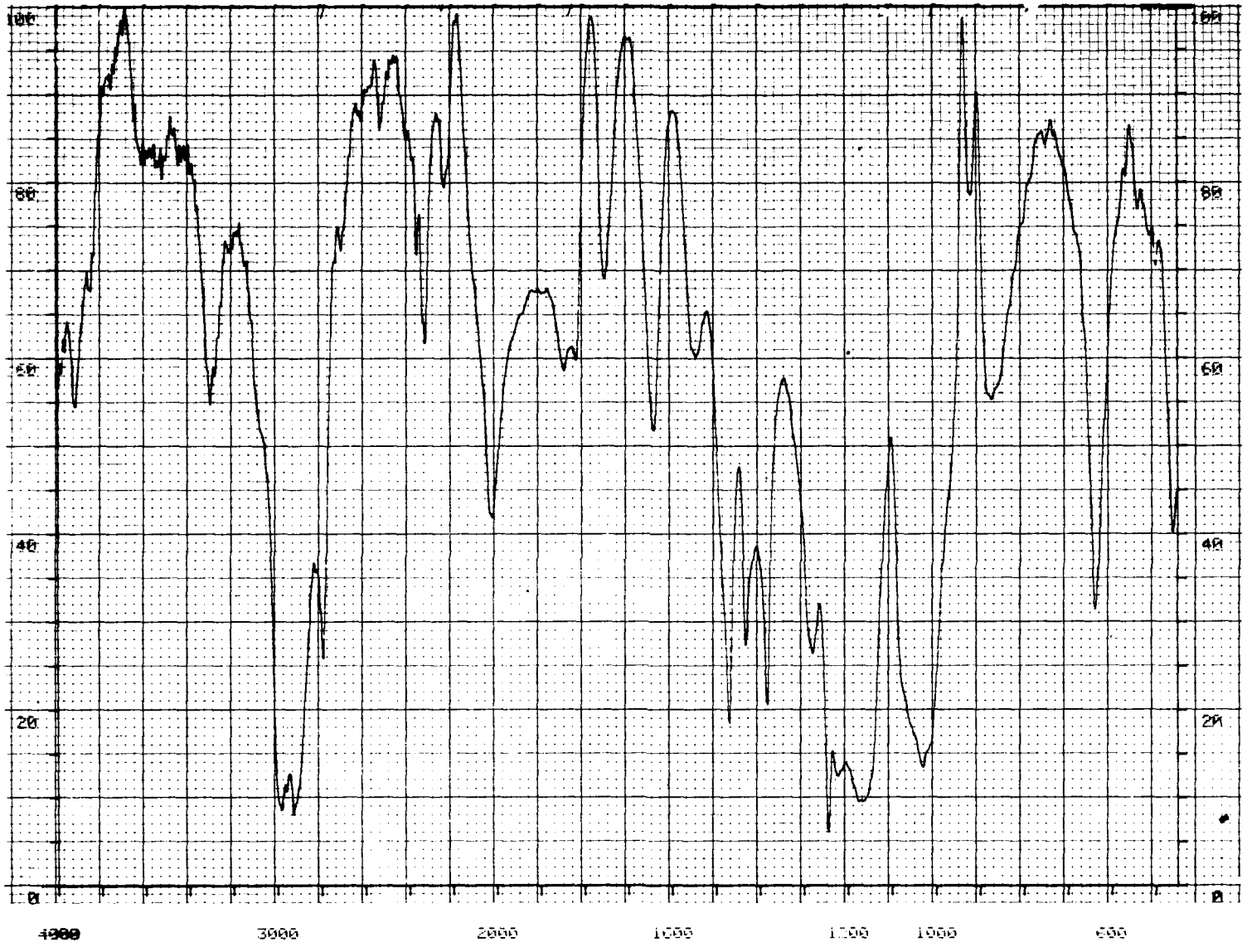


Figure 10. Infrared spectrum of white obturator by diffuse reflectance (shavings)

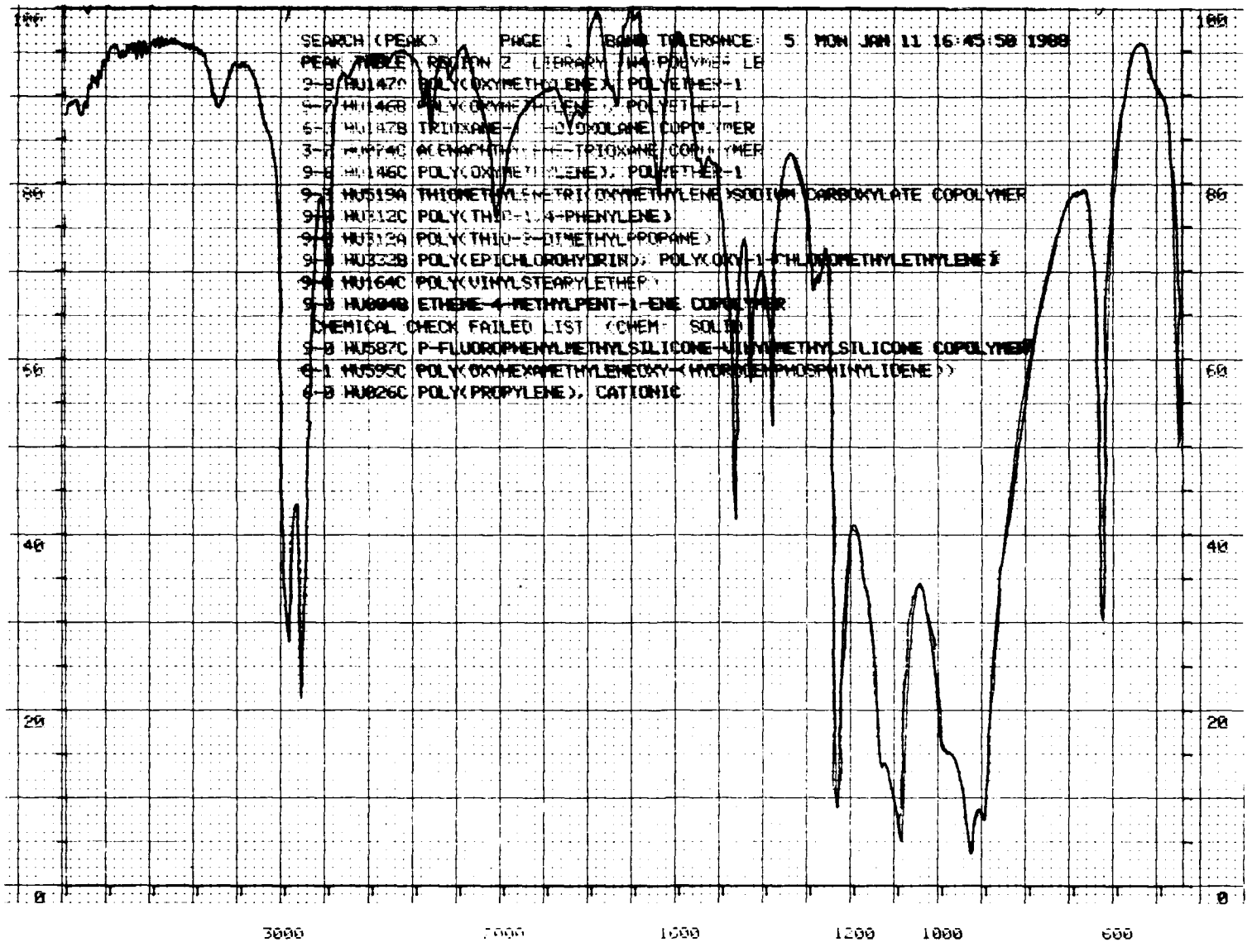


Figure 11. Infrared spectrum of white obturator (hot melt smear on KRS-5 crystal)

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